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Task I - Silicon Material

Gaseous Melt Replenishment System

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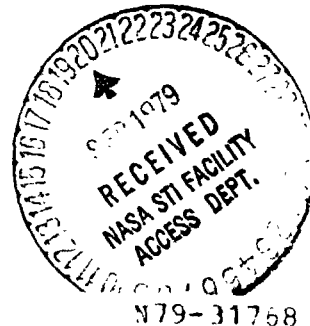
JPL Contract 955269

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### ABSTRACT

This program was initiated in April of this year to develop a system to combine silicon formation, by hydrogen reduction of trichlorosilane, with the capability to replenish a crystal growth system. The silicon formation system is based on a resistance heated quartz reaction vessel in which reduction of trichlorosilane deposits silicon on the walls of the vessel. After sufficient deposition has occurred, the silicon will be melted out of the reaction vessel and carried to the crystal growth system by a heated quartz delivery tube. Isolation of the reaction vessel during the silicon formation stage will be accomplished by a quartz U-tube trap-type valve containing silicon which can be melted to allow passage of molten silicon, or solidified to prevent passage of reactant gases.

During the quarterly reporting period, we have estimated a variety of process parameters to allow sizing and specification of gas handling system components. Most of the major components of the system have been designed, or specified, and ordered.

## I. INTRODUCTION

This program is intended to develop a system which incorporates both silicon formation and melt replenishment into the same piece of equipment. The processes and equipment are scaled such that a modest investment can make available to the Czochralski crystal grower a low cost source of silicon. In addition, the smaller scale of operation means that the systems can be put into operation without large capital investments, guaranty of markets, etc.

The chemical reactions,  $H_2$  reduction of  $SiHCl_3$ , are those in commercial usage now. The major innovation is in reactor design which allows a high productivity of silicon. The reactor has been conservatively sized on the basis of epitaxial deposition rates. The conclusion of this calculation is that a reasonably sized system can produce silicon rapidly enough to keep pace with either 10 cm or 12 cm diameter Czochralski crystal growth operating in a semi-continuous mode.

The program plans call for design, construction and testing of a prototype system and demonstration, over a twenty-four hour period, of a 0.5 kg/hr rate of Si production with 18% conversion efficiency. Based on initial findings with the prototype system,

a second generation system will be built and demonstrated over a 96 hour continuous run. This system will also include a valve/delivery tube system to allow replenishment of a crystal growth system. Demonstration of the complete system performance in operation with a Czochralski crystal puller over a 96 hour period will comprise the final phase of the program.

## II. PROCESS DESCRIPTION

A schematic cross-section of the reactor system is shown in Figure 1. Polycrystalline silicon will be deposited on the inside walls of a resistively heated, multi-walled fused silica reaction chamber by  $H_2$  reduction of  $SiHCl_3$ . After sufficient silicon has been produced, the reactor is flushed with argon and the silicon melted out of the reactor into a Czochralski crystal growth crucible. The reactor is then returned to the deposition stage. The reaction chamber and the crystal growth system are separated by a heated delivery tube. The "U" tube acts as a valve by adjusting the temperature above or below the melting point of silicon. A more detailed description of a process cycle is given below:

1. The reactor is brought up to temperature under inert gas flow.
2. A small amount of silicon is melted in the "U" tube to form a positive gas seal. The "U" tube temperature is dropped to about  $1200^{\circ}C$ .
3. At the selected reaction temperature  $SiHCl_3$  and  $H_2$  are introduced into the chamber and their flow rates set to optimize the maximum mass deposition of silicon.

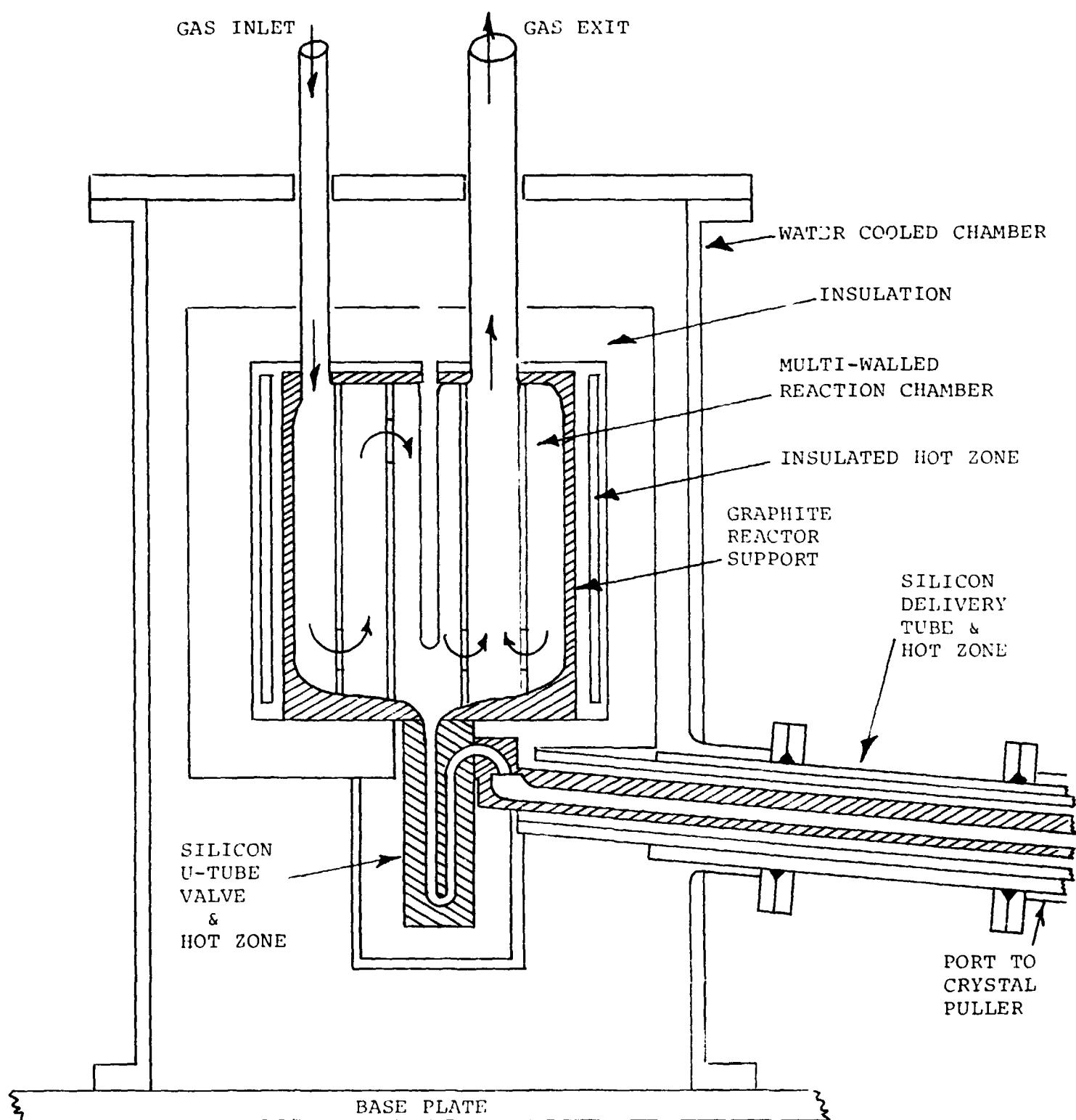


Figure 1.

Schematic Diagram of  
"Poly" Reaction Chamber

(Scale  $\approx 5:1$ )



4. The reaction is allowed to run for several hours until the desired amount of silicon has been deposited. This is determined by the desired cycle time and the reactor vessel size.
5. At this point the reactant gases are flushed out of the reactor with Ar.
6. Keeping the "U" tube at 1200°C, the reactor is raised to about 1450°C to melt down the silicon produced.
7. The gas pressure between the reactor and the delivery tube is equilibrated.
8. The "U" tube and delivery tube are raised to about 1415°C. When the silicon is melted in the "U" tube, the reactor will empty due to gravity, causing liquid silicon to flow out through the delivery tube to either the Czochralski crucible or an intermediate replenishment crucible. Due to the equilibrated pressures and a vent to prevent siphoning, the "U" tube will remain full after the reactor has been emptied.
9. The reactor is returned to reaction temperature and the "U" tube and delivery tube are returned to 1200°C.
10. The reactant gas flow is then re-admitted to the chamber to start the cycle again.

### III. DISCUSSION

#### A. System Design Considerations

The prototype system is being designed to yield a rate of Si formation of at least 0.5 kg/hr, with an assumed conversion efficiency of 30%. This yield we believe to be attainable based on reported efficiencies in an open flow-through tube reactor of 28% (1) and 50% in a fluidized bed system. (2) These assumptions lead to the typical reactant and product quantities listed in Table I.

Data from the work of Hunt, Sirtl, and Sawyer (3,4) have provided the basis for most of our calculations, recognizing that their data are equilibrium values. Using  $\text{SiHCl}_3$  as the silicon source, we have replotted data of Hunt, *et. al.* to indicate the potential conversion of silicon in the gas at various hydrogen dilutions (Cl/H ratio) over a range of temperatures, Figure 2. In Figure 3 we have plotted, based on a silicon formation rate of 0.5 kg/hr, from  $\text{SiHCl}_3$ , the volumetric flow rate of reactants as a function of temperature for various Cl/H ratios. This allows estimation of the minimum flow likely to be encountered over a variety of conditions. Our intent for the prototype system has been to try to design and choose the

Table I

Reactant and Product Quantities:  
0.5 Kg/hr. Deposition Rate, 30% Yield

<u>Species</u>	<u>Moles</u>	<u>Weights, kg</u>	<u>Volume (STP) ft<sup>3</sup></u>	<u>Volume (1300°K)</u>
<u>Reactants:</u>				
SiHCl <sub>3</sub>	59	7.99	47	222
H <sub>2</sub>	395	0.80	312	1489
			Total	1710
<u>Products:</u>				
SiHCl <sub>3</sub>	13	1.76	10	38
SiCl <sub>4</sub>	28	4.78	22	83
HCl	25	0.91	20	75
H <sub>2</sub>	404	0.81	319	1202
Si (s)	17.8	0.5	-	-
			Total	1400

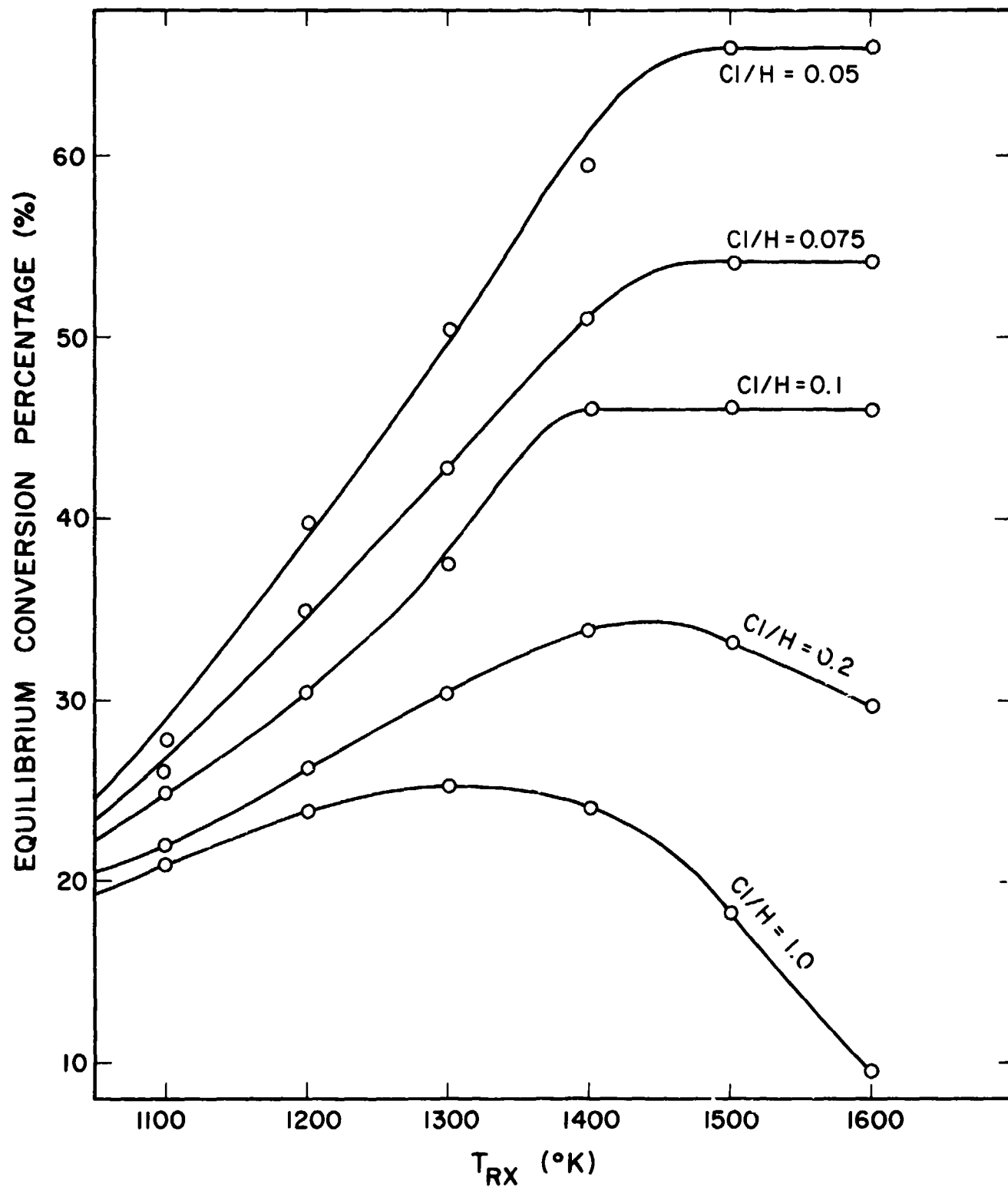


FIGURE 2. CONVERSION EFFICIENCY FROM  $SiHCl_3$  AT VARIOUS  $H_2$  DILUTIONS AS A FUNCTION OF TEMPERATURE. AFTER REF. 3, FIG. 3.

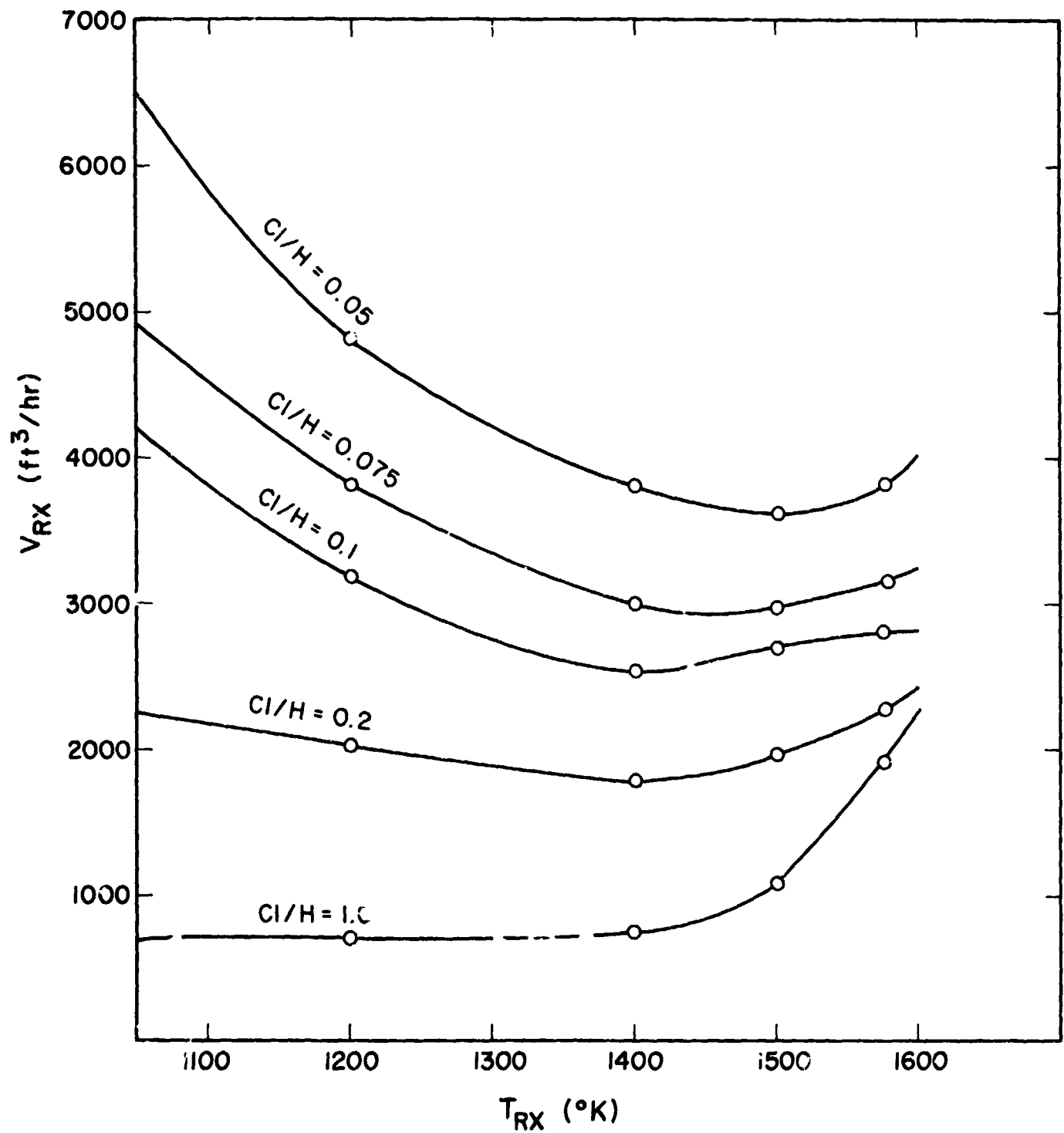


FIGURE 3. TOTAL GAS FLOW RATE TO YIELD 0.5 KG/HR OF SI AT VARIOUS  $\text{H}_2$  DILUTIONS OF  $\text{SiHCl}_3$  AS A FUNCTION OF REACTION TEMPERATURE. AFTER REF. 3.

various components to ensure adequate flexibility to permit operation of the system over a range of conditions. Since we are not sure of the parameters which will lead to maximum production rates, we must necessarily be able to operate the system experimentally under different conditions.

Calculations of the energy requirements of the prototype system indicated that effective heat transfer to the reactor inlet stream, of  $H_2$  and  $SiHCl_3$ , from the product stream can yield significant energy savings, as well as more rapid and complete reaction of the inlet gases. Table II lists, calculated on the same basis as the example of Table I, the approximate energies required to heat the reactant gases to the reaction temperature, to carry out the reduction of part of the trichlorosilane, to melt the deposited silicon, and to maintain the reactor at temperature. The energy required to heat the reactant gases is seen to comprise approximately 40% of the total energy; it is also the only energy input which offers the possibility of useful recovery. Preheating of the reactant gases is also seen as a means to ensure a closer approach to equilibrium and higher yield in the reactor, by bringing the gas stream to as high a temperature as possible, as soon as possible, thus allowing a greater fraction of the residence time for reaction at temperature.

#### B. EQUIPMENT

Figure 4 is a schematic diagram of the gas handling system and reactor. The system essentially consists of a stream of circulating hydrogen to which  $SiHCl_3$  is added, a fraction of

Table II

Process Heat Requirements: 0.5 kg/hr, 30% yield

	<u>Energy Input, KW/hr.</u>
Inlet gas enthalpy (R.T. to 1300°K): H <sub>2</sub> (312 CFH,STP)	3.2
SiHCl <sub>3</sub> (47 CFH,STP)	1.6
	<hr/> 4.8
Reaction Heat (Stoichiometry of Table I):	(-0.2)
Reactor furnace heat loss @ 1300°K (estimated):	6.0
Silicon Meltdown heat (estimated):	2.5
	<hr/>
Approximate total required/hr.	13.1

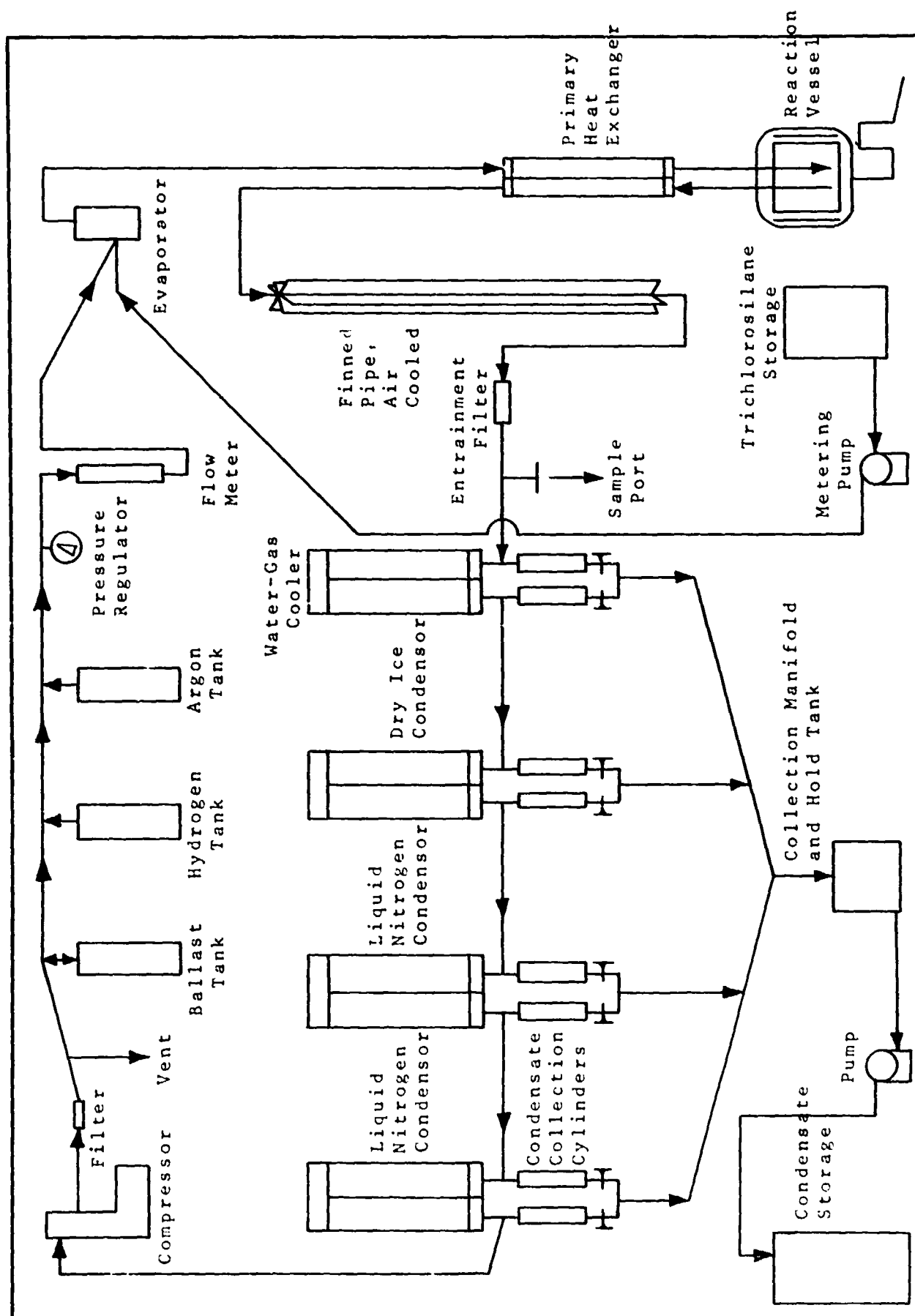


FIGURE 4. SCHEMATIC DIAGRAM OF PROCESS EQUIPMENT AND FLOW SYSTEM.



which is then removed by conversion to solid Si,  $\text{SiCl}_4$ , and possibly  $\text{SiH}_2\text{Cl}_2$  in the reactor, and which is subsequently cooled and purified by condensation of the chlorosilanes and removal of HCl. Thus, a number of basic features of the system are determined. A recirculating pump, make-up hydrogen, storage and pressure ballasting tank, trichlorosilane liquid metering pump and evaporator provide the mixture of reactants to the deposition reactor. After reaction/deposition the gas stream is cooled to remove the chlorosilanes and HCl. Because of the fairly low concentrations of chlorosilanes, the gas stream will need to be cooled to lower temperatures than indicated by the boiling points of the pure materials.

#### 1. Trichlorosilane Evaporator

We have decided to use an evaporator configuration similar to a vacuum diffusion pump operating in reverse. Trichlorosilane liquid, fed by a Teflon diaphragm metering pump, will be mixed with the hydrogen stream in the "foreline". The gas-liquid mixture passes into the heated, lower section of the evaporator and out the top. If necessary, baffles may be installed in the evaporator to prevent liquid entrainment and to improve gas mixing. We intend to heat, and insulate, the gas stream from the evaporator into the primary heat exchanger. The evaporator will be fabricated from carbon steel and be demountable and readily disassembled for cleaning.

#### 2. Primary Heat Exchanger

As noted above we have considered exchange of heat between reactant and product streams to be important both chemi-

cally and economically. Thus we have designed a heat exchanger for the reactor process stream.

Trichlorosilane data from the Lamar University Group's Quarterly Report (XIII) (5), silicon tetrachloride data from "Physical and Thermodynamic properties of Silicon Tetrachloride" by Yaws, et. al (6); and hydrogen and hydrogen chloride data from "Heat Exchanger Design" by Fraas and Ozisik (7) were used to calculate the gas stream mixture properties relevant to design of the exchanger. These gas properties for specific geometric exchanger designs were used to calculate the gas boundary layer thickness,  $\delta$ , which limits heat transfer, the bulk stream heat transfer coefficient,  $U$ , was then determined from the calculated values of  $h$  and  $\delta$ . Reynolds numbers were also calculated which indicate slightly turbulent flow through the exchanger. The overall transfer coefficient,  $U$ , was then used to determine the surface area needed for required temperature changes, and flow rates. Several trial calculations were done to determine the exchanger design for the system to be tested.

The exchanger will be made of graphite. The hot outlet gases will split to flow in two streams on either side of the inlet gas. The gas stream will be separated by finned transfer plates. Fins 0.1 inch thick, 0.1 inch apart, and 0.45 inches high will be machined into either side of the transfer plates. The exterior surfaces will be plain graphite plates and the complete exchanger will be insulated and enclosed in an argon-purged metal enclosure. The exchanger will be approximately 4" x 3" x 20" overall. The design performance of the

exchanger is as follows: inlet stream temperature will be raised from 60°C to 700°C, while the outlet stream will drop from 1100°C to 350°C. The heat transfer surface area is approximately 7 ft<sup>2</sup>, and the overall transfer coefficient will vary with mass flow rate from approximately 3 to 7 BTU/hr ft<sup>2</sup> °F. Our present intention is to connect the quartz tubulations of the reactor vessel directly to the heat exchanger using metal graphite compression seals with Grafoil® gaskets.

### 3. Reactor Furnace/Enclosure

The configuration chosen for the furnace enclosure is a vertical cylindrical chamber with domed ends. The chamber is split horizontally slightly above the mid-line to allow the one-piece top half to be lifted up, while the bottom section is flanged at the dome, but will ordinarily remain in place as the support for all the hot zone parts. Flanged ports 10 and 12 inches I. D. will be provided in the top and bottom respectively. The inner shell will be stainless steel and the outer shell and flanges will be carbon steel.

The furnace, proper, will be constructed from graphite sheet and Grafoil® heating elements, surrounded by graphite felt insulation. The U-tube valve, attached to the bottom of the reactor, will be similarly heated.

### 4. Reactor Vessel

The deposition reactor will be a box-like quartz structure with internal plates for greater surface area and to provide different gas flow paths. The reactor geometries illustrated in Figure 5 represent two of the geometries we intend to

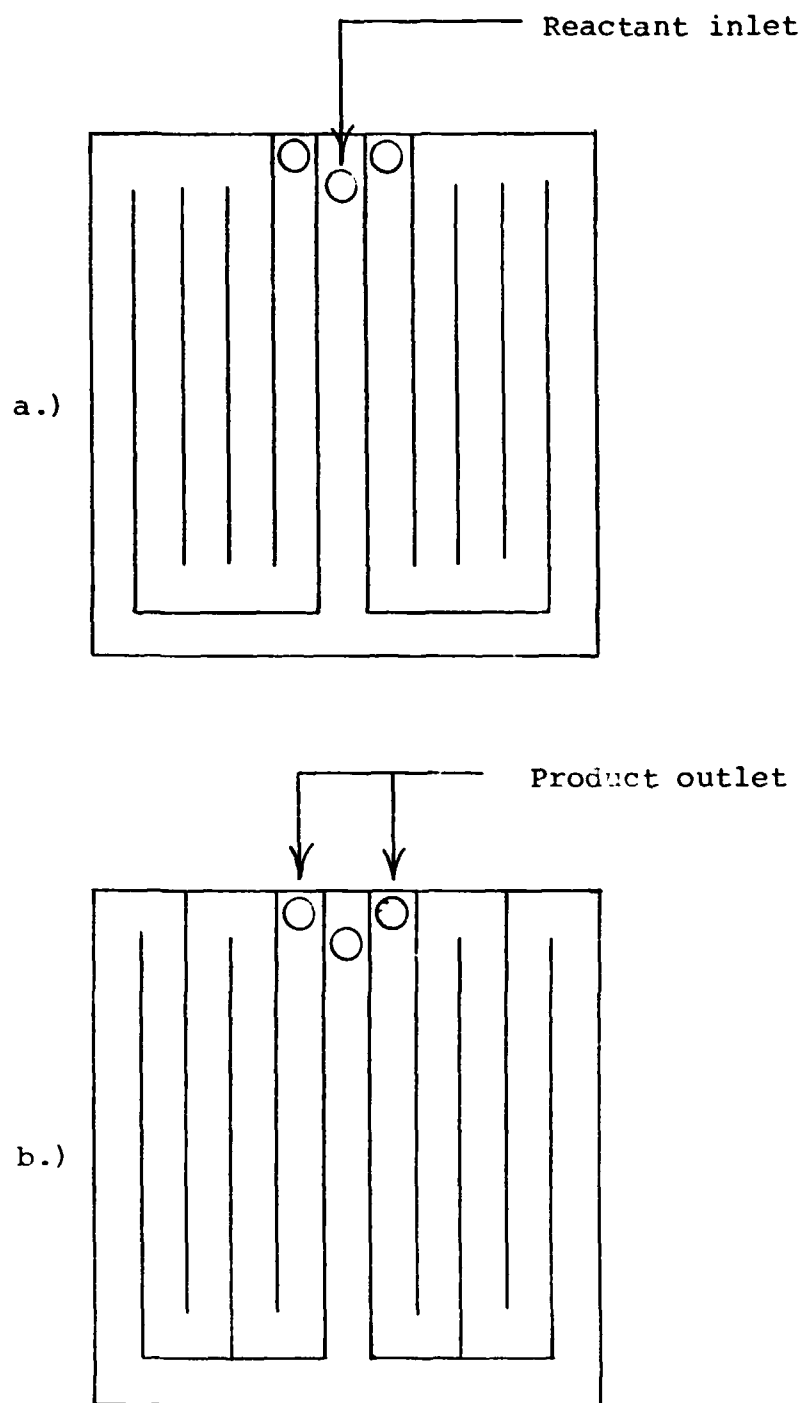


FIGURE 5. SCHEMATIC PLAN SECTION VIEW OF INITIAL REACTOR GEOMETRIES. A.) PARALLEL PLATE, LOW VELOCITY,  $N_{RE} \approx 200$ . B.) SERIES PLATE, HIGH VELOCITY,  $N_{RE} \approx 700$ .

test in the initial optimization experiments. These reactors will have approximately equal internal surface areas, while the gas flow velocity will differ by a factor of approximately three ( or four if extra plates are used) between the parallel flow (Fig. 5a) and series flow (5b) arrangements. Both of these geometries should operate in a laminar flow regime based on approximate sizes and the volumes of Table I. A third geometry, not shown, will consist of staggered tee or chevron baffles, arranged to produce turbulent flow and to enhance fine particle collection by impact.

A secondary, high temperature heat exchanger arrangement has been conceived as an integral part of the internal structure of the reactor vessel. The exiting gas in the reactor will flow on both sides of the entering stream, which has been pre-heated in the primary heat exchanger. The principal function of this exchanger is seen as bringing the inlet stream rapidly up to temperature to maximize Si deposition, while on the outlet side, the gas temperature will be reduced, thus ensuring against deposition outside the reactor, in the primary heat exchanger.

#### 5. Product Stream Treatment and Analysis

We have considered a variety of methods of treating the product stream. In the prototype system it is desirable to separate the hydrogen from the chlorosilanes and hydrogen chloride in order to provide a straight forward input gas mixture of measured quantities of  $H_2$  and  $SiHCl_3$ . In a production system it is likely that the chlorosilanes would be recirculated with the hydrogen, although it would still be necessary to remove  $HCl$ , which

otherwise tends to push the reduction reaction backwards.

The prototype system is designed to cool the product gases, condense out the chlorosilanes, and remove hydrogen chloride by absorption on activated carbon. There is also provision made to pass the stream through a high temperature filter, before going into the condensers, to look for entrained silicon powder formed by gas phase reaction in the reactor. (Balston Filter Model 20/35A; Type DH, inorganic bonded glass fiber filter 2 inch diameter by 9 inches long.)

Condensation of the chlorosilanes will be accomplished by passing the stream through shell and tube heat exchangers cooled successively by water, dry ice/methanol, and liquid nitrogen.

Analysis of the product stream is also needed to provide fairly rapid feedback with respect to deposition rates and efficiency, without having to melt out the deposited silicon after each run with a given set of conditions. We are planning eventually to incorporate a gas chromatograph into the product gas line to provide essentially on-line analysis.

Initially we plan to characterize the chlorosilane products after condensation and collection by density measurement on a known sample volume. This, in conjunction with measurement of the rate of collection of  $\text{SiCl}_4$  and  $\text{SiHCl}_3$ , should give reasonably accurate values for the reaction rate and the deposition efficiency, in the absence of significant formation and carry-over of other silicon chlorides.

## 6. H<sub>2</sub> Recirculation Pump

We have chosen a compressor for recirculating the hydrogen stream which is specifically designed for oil-free, dry pumping of corrosive gases. (Model 490, Corken Pump Co., 5:1 compression ratio, 13-36 CFM displacement). The pump uses Teflon piston rings and seals.

Hydrogen input flow will be measured by a Brooks Rotameter Model 1110, 2.2 - 22 CFM flow range, accuracy  $\pm 2\%$ . Filtration of the hydrogen stream will be by a Balston Type 45, stainless steel bodied filter with a 1" x 7" filter element of epoxy-bonded borosilicate glass fibers.

## 7. Safety Systems

The entire gas handling and reactor system will be enclosed under a vented hood to remove irritating and potentially explosive gases in the event of leaks.

Purging and venting of the system will be by argon, and these gases will be passed through a limestone and trickling water scrubber before venting to the atmosphere.

Preliminary consideration has been given to a system which will allow rapid equilibration of the pressure inside the reactor with that in the reactor furnace enclosure. Effective operation of this system will eliminate the possibility of explosion or implosion of the reactor. We have not yet decided on a simple, failsafe means of accomplishing this, although several more or less complicated ways are obvious. It is apparent that initial testing and adjustments to the gas system will be carried

out with a metal surrogate reactor, fitted with a differential pressure gauge and using inert gas.

#### IV. PROJECTED SECOND QUARTER ACTIVITIES

Planned activities for the second quarter (July-October) include:

- Complete design, construction and installation of the prototype reactor system.
- Start-up operation and initial experimental runs with the prototype system.



V.     REFERENCES

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PROGRAM PLAN - Milestone Chart - (JPL Contract 955269)

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